The Chemical Diffusivity of Oxygen in Liquid Iron Oxide and a Calcium Ferrite

Y. LI, J.A. LUCAS, R.J. FRUEHAN, and G.R. BELTON

Measurements have been made of the chemical diffusion coefficient of oxygen in liquid iron oxide at temperatures from 1673 to 1888 K and in a calcium ferrite (Fe/Ca = 2.57) at temperatures from 1573 to 1873 K. A gravimetric method was used to measure the oxygen uptake during the oxidation of the melts by oxygen or CO_2-CO mixtures. The rate was shown to be controlled by mass transfer in the liquid melt. The chemical diffusivity of oxygen in liquid iron oxide at oxygen potential between air and oxygen was found to be $4.2 \pm 0.3 \times 10^{-3}$ cm²/s at 1888 K. That in iron oxide at oxidation state close to iron saturation was established to be given by the empirical expression $\log D = -6220/T + 1.12$ for temperatures between 1673 and 1773 K. For the calcium ferrite (Fe/Ca = 2.57) at oxygen potential between air and oxygen, the diffusivity of oxygen was found to be given by $\log D = -1760/T - 1.31$ for temperatures between 1673 and 1873 K.

I. INTRODUCTION

AN understanding of the overall rate of reduction or oxidation of iron oxide from an iron oxide-containing slag requires a knowledge of the transport properties of iron oxide in the slag.[1,2] Recent studies by Xie and Belton[3] showed that the chemical diffusivity of iron oxide in $40CaO$-$40SiO_2$-$20Al_2O_3$ slags increases with increasing concentration of iron oxide. They also found evidence that the chemical diffusivity of iron oxide in calcium silicate and calcium aluminosilicate slags, containing relatively low concentrations of iron oxide, increases with the state of oxidation. As a limiting case, the diffusivity of oxygen in liquid iron oxide and its dependence on the state of oxidation is of obvious interest. Calcium ferrite is an important slag system in iron-making and nonferrous metallurgical processes. The addition of calcium oxide to liquid iron oxide was found to increase the reduction rate of iron oxide by an order of magnitude.[4,5] A comparison of the diffusivity of oxygen in calcium ferrite and that in pure liquid iron oxide may also shed some light on the mechanism of the diffusion.

The limited reported values for the chemical diffusivity of oxygen in pure liquid iron oxide[6,7,8] differ by two orders of magnitude. Grieveson and Turkdogan[6] studied oxidation and reduction of liquid iron oxide by CO_2-CO mixtures at 1823 K. It was assumed that the diffusion in the melt was the rate-limiting step. The value of the interdiffusivity of oxygen and iron, thus, obtained was $5(\pm 1) \times 10^{-5}$ cm²/s. Further work by Mori and Suzuki[7] determined the diffusivity in liquid iron oxide over a wider composition range within a temperature range of 1703 to 1823 K using a similar experimental technique. At 1823 K, the interdiffusivity was found to decrease from about 4×10^{-4} to 5×10^{-5} cm²/s as $Fe^{3+}/\Sigma Fe$ increased from 0.12 to 0.42. The activation energies for diffusion were found to be about 46 and 71 kJ/mol at $Fe^{3+}/\Sigma Fe$ of 0.12 and 0.33, respectively. With more accumulated data[9,10] on the *chemical* reaction rate at the interface between a slag and CO_2-CO gases, Belton[11] has analyzed Grieveson and Turkdogan's[6] data and has shown that the rate measured by Grieveson and Turkdogan could well be under the control of the slow gas-slag chemical reactions. Recognizing the possible limitation of the slow interfacial chemical reaction between iron oxide and CO_2-CO gases, Sayadyaghoubi *et al.*[8] recently studied the chemical diffusivity of oxygen in liquid iron oxide by oxidizing the melt with pure oxygen. The chemical reaction rate of the oxidation of the melt by oxygen was belived to be much faster than that by CO_2 and was, thus, ruled out from the rate controlling steps. The average value of the chemical diffusivity of oxygen in liquid iron oxide with $Fe^{3+}/\Sigma Fe$ between 0.25 and 0.77 was found to be $3(\pm 1) \times 10^{-3}$ cm²/s. This value is one to two orders of magnitude higher than those obtained in earlier studies.

Strachen[12] studied the interdiffusion coefficients in molten calcium ferrites. Diffusivity values as high as 10^{-2} cm²/s have been reported.[13] The diffusivity was found to increase with increasing concentration of calcium oxide and, at a given concentration of CaO, with the $Fe^{3+}/\Sigma Fe$ ratio.

In all the diffusion measurements mentioned previously, the diffusivity was evaluated from the variation of the Fe^{3+}/Fe^{2+} ratio, hence oxygen concentration, with time by analyzing the quenched slag either as a whole or as transverse layers. This method is an *indirect* measurement of the oxygen uptake. Error may be introduced by concentration (and concentration profile) changing during quenching, sectioning, and chemical analysis. In the present study, direct and *in situ* measurements of the oxygen uptake during oxidation were made by continuously monitoring the weight change of the sample. The present study was undertaken to (1) resolve the differences among the reported values of diffusivity of oxygen in liquid iron oxide; (2) study the effect of oxidation state on the diffusivity; and (3) determine the diffusivity of oxygen in a calcium ferrite.

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II. EXPERIMENTAL DETAILS

A. *Principle of the Measurement of Diffusivity*

Two methods, namely, non-steady-state and steady-state diffusion involving the gas-melt reaction, were used in the present study. The non-steady-state method was used to measure the chemical diffusivity of oxygen in melts at high oxidation state close to pure oxygen. In this method, a crucible of uniform diameter with one end sealed was filled with the melt and pre-equilibrated in a gas mixture of known oxygen potential. At this stage, a uniform concentration of oxygen (or Fe^{3+}, Fe^{2+}), C_0, was established throughout the melt. The reacting gas mixture was then changed to another one of higher oxygen potential. By doing this, the concentration of oxygen at the surface of the melt was fixed at another value C_s. Oxygen will, thus, diffuse into the melt, and the diffusivity can be evaluated from the weight change of the sample. If the diffusion is treated as a unidirectional diffusion in a semi-infinite medium, the weight gain of the sample during oxidation takes the form

$$M_t = \frac{2A(C_s - C_0)}{\sqrt{\pi}} \sqrt{Dt} \qquad [1]$$

where

M_t = the sample weight gain from $t = 0$ to $t = t$ (g);
C_s = the concentration of oxygen in the melt at the gas-melt interface (g/cm³);
C_0 = the initial concentration of oxygen in the melt (g/cm³);
A = is the surface area of the melt (cm²);
t = is time (s); and
D = is the diffusivity (cm²/s).

The concentration of oxygen in the melt can be calculated as

$$C = \rho \, \frac{3\dfrac{Fe^{3+}}{Fe^{2+}} + 2}{10\dfrac{Fe^{3+}}{Fe^{2+}} + 9} \qquad [2]$$

where ρ is the density of the melt in g/cm³, and Fe^{3+}/Fe^{2+} is the ferric/ferrous ratio in the melt. Equation [1] shows that the plot of weight gain (M_t) against the square root of the time ($\sqrt{t}$) will yield a straight line with a slope of $2A(C_s - C_0)(D/\pi)^{0.5}$. The diffusivity, D, can be evaluated from this slope given the information of the area, density of the melt, initial, and surface Fe^{3+}/Fe^{2+} ratio in the melt.

One of the disadvantages of this method is the requirement of information on the oxygen concentrations (*i.e.*, the Fe^{3+}/Fe^{2+} ratios) equilibrated with P_{O_2} used in the experiment. Unfortunately, gas-melt equilibrium data on liquid iron oxide at high oxygen potentials are scarce and inaccurate due to experimental difficulties.[14] Another problem with this treatment is that the semi-*infinite* assumption is difficult to satisfy in a real experiment, especially for melts with high diffusivities.

Alternatively, the diffusion may be treated as unidirectional diffusion in a finite medium (as it is in practice), and the diffusivity was evaluated from the fractional weight change (M_t/M_∞) *vs* time curve. If M_t denotes the total amount of diffusing substance that has entered the melt at time t, and M_∞ the corresponding quantity after infinite time, then[15]
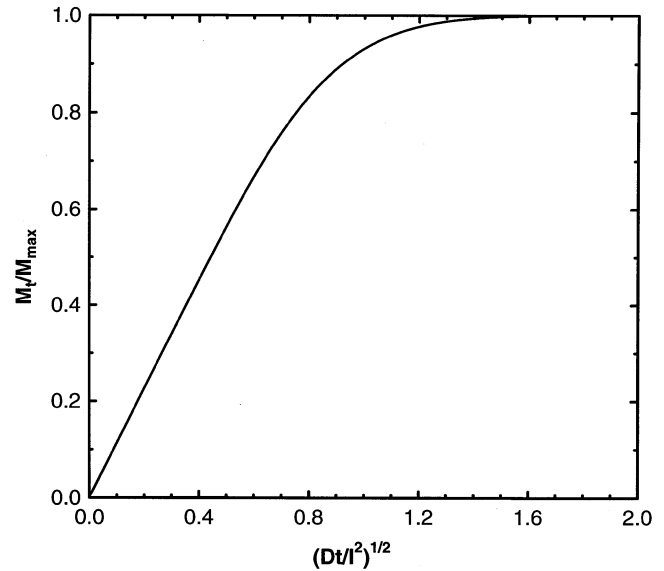

Fig. 1—Calculated uptake of oxygen by the melt of l in depth during oxidation.

Table I. Calculated Values of the $(Dt/l^2)^{1/2}$ Corresponding to Several M_t/M_∞ Ratios

M_t/M_∞	0.2	0.3	0.4	0.5	0.6	0.7	0.8
$(Dt/l^2)^{1/2}$	0.178	0.266	0.355	0.444	0.536	0.635	0.754

$$\frac{M_t}{M_\infty} = 1$$
$$- \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \, \pi^2} \exp\left\{ \frac{-D(2n+1)^2 \pi^2 t}{4l^2} \right\} \qquad [3]$$

where l is the depth of the melt.

Equation [3] shows that the M_t/M_∞ ratio is a function of diffusivity D, the depth of the melt l, and time t, *not on* the initial and surface oxygen concentration. Experimentally, the maximum weight change M_∞ can be determined by extending the oxidation for a long period of time until the weight *vs* time curve levels off. After obtaining the M_t/M_∞ *vs* time curve, the only information required to determine the diffusivity is the depth of the melt l. A numerical calculation for Eq. [3] was carried out, and a graph of M_t/M_∞ as a function of $(D_t/l^2)^{1/2}$ is shown in Figure 1. The values of the $(D_t/l^2)^{1/2}$ corresponding to several M_t/M_∞ ratios are listed in Table. I. The experimentally determined M_t/M_∞ *vs* time curve can be used to determine the time required to reach these M_t/M_∞ ratios, and the diffusivity can, thus, be evaluated using the data in Table I and the depth of the melt.

The steady-state method was used to measure the chemical diffusivity of oxygen in iron oxide at a low-oxidation state close to iron saturation. In this method, a pure iron disc was placed at the bottom of the crucible, and the liquid iron oxide above the disc was equilibrated with the metallic iron in purified nitrogen. At this stage, a uniform concentration of oxygen (or Fe^{3+}, Fe^{2+}), C_0, was established throughout the melt. The gas was then changed to a $CO-CO_2$ mixture of known composition. By doing this, the concentration of oxygen at the surface of the melt was fixed at another value
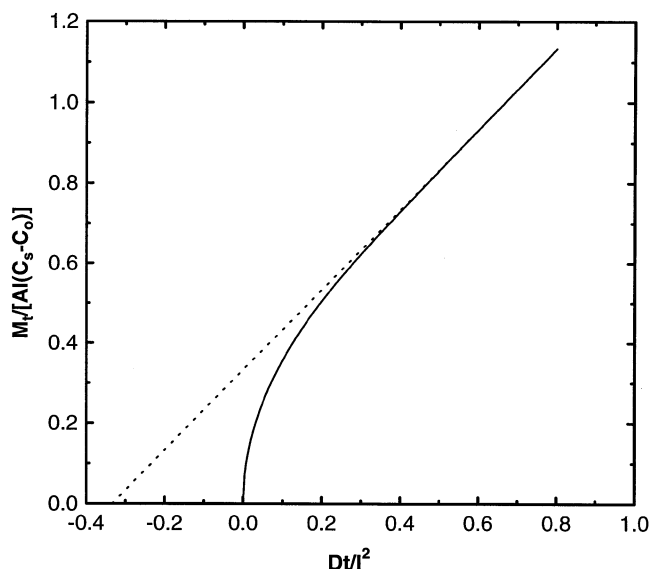
Fig. 2—Approach to steady-state diffusion of oxygen through a melt of l in depth.

C_s. Oxygen will, thus, diffuse into the melt, and the weight gain of the sample is given by the equation

$$M_t = DA \frac{C_s - C_0}{l} \left(t + \frac{l^2}{3D} \right)$$ [4]

$$- \frac{2(C_s - C_0)lA}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-Dn^2\pi^2 t}{l^2} \right)$$

As $t \rightarrow \infty$, M_t approaches the line

$$M_t = DA \frac{C_s - C_0}{l} \left(t + \frac{l^2}{3D} \right)$$ [5]

This line has a slope of $DA(C_s - C_0)/l$. The diffusion constant, D, can be evaluated using the steady-state slope of the M_t vs t plot. In this case, we need to know, in addition to the weight (of the substance transferred to the melt) vs time curve, the inner diameter of the tube, d, concentrations at both the surface and the bottom of the melt, C_s and C_0, and the depth of the melt, l.

The line described by Eq. [5] has an intercept t_0 on the t-axis given by

$$t_0 = -\frac{l^2}{3D}$$ [6]

Equation [6] can be used as an alternative way to evaluate the diffusion constant D. Having the experimentally obtained w vs t curve, the only additional information needed to evaluate D by this method is the depth of the melt, l.

Numerical calculation was carried using Eq. [4], and the results are shown in Figure 2 where the dimensionless total uptake, $M_t/[lA(C_s - C_0)]$, is plotted against the dimensionless time, Dt/l^2.

B. *Experimental*

The experimental setup is schematically shown in Figure 3. The molybdenum-wound resistance furnace was equipped with a 52-mm inner diameter alumina working tube, and
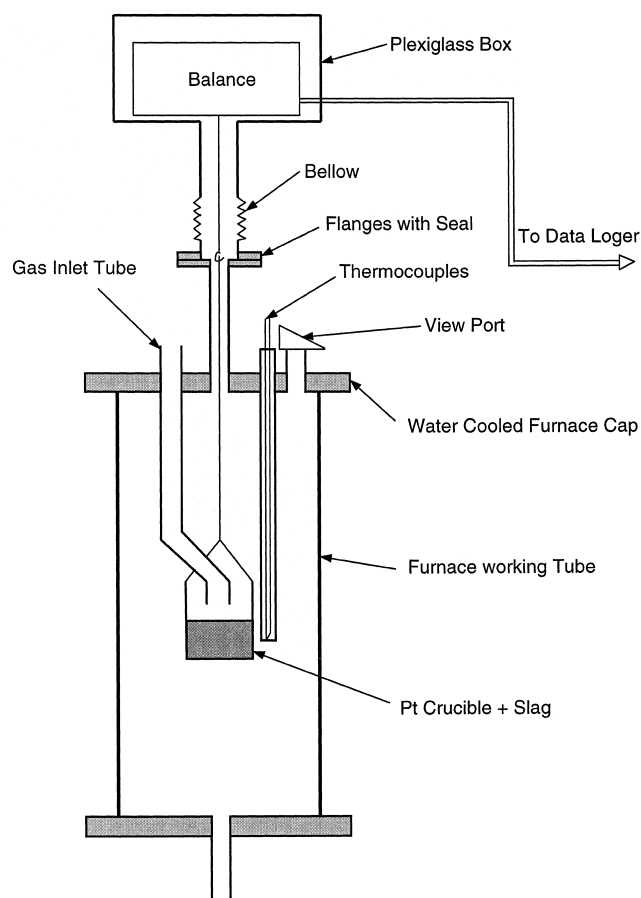

Fig. 3—Schematic diagram of the experimental setup.

the temperature was controlled by an Eurotherm (Eurotherm Controls, Inc., Reston, VA) controller with a Pt-6 pct Rh/Pt-30 pct Rh (type B) thermocouple located close to the sample. The temperature profiles in the working tube were measured under the same experimental conditions, such as mass of the sample and the gas flow condition, as those used in the diffusivity measurement experiments. A hot zone 50-mm long was obtained in which the temperature varied less than ± 1 K. The location of the sample in the hot zone was such that the top of the melt was slightly hotter (approximately 1 K) than the melt at the bottom. This temperature gradient prevented convection in the melt due to the density gradient. A platinum crucible or magnesia crucible containing the slag was placed inside a 20-mm-i.d. by 50-mm-long porous magnesia crucible, which was attached to the balance by means of a platinum wire. The electrobalance (connected to a PC for data logging) was accurate to ± 0.1 mg. The gas delivery tube was a high purity transparent silica tube of 10-mm o.d. and 8-mm i.d. It was located so that its exit was 10 to 15 mm above the surface of the melt.

Gases used in the experiments were CO (99.97 pct), CO_2 (99.9 pct), N_2 (99.999 pct), air, and O_2 (99.99 pct) supplied by Linde Gas (Sydney, Australia). All the gases were passed through Dryerite (Drierite Co., Xenia, OH) ($CaSO_4$), to remove moisture, and through Ascarite (granulated sodium hydroxide on support) to remove CO_2. Nitrogen was further purified by passing through copper turnings at 873 K and magnesium turnings at 723 K to remove trace amounts of oxygen. The gas flow rates were controlled by a set of mass
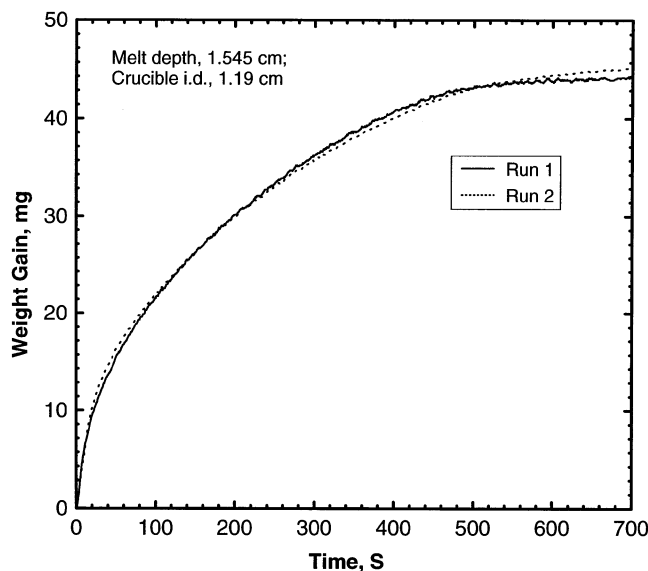
Fig. 4—Weight change during oxidation of liquid iron oxide pre-equilibrated in air and oxidized in pure oxygen at 1615 °C. Melt depth, 1.545 cm; crucible i.d., 1.19 cm; iron oxide (as Fe_2O_3) weight, 7.936 g; and gas flow rate, 600 SCCM.
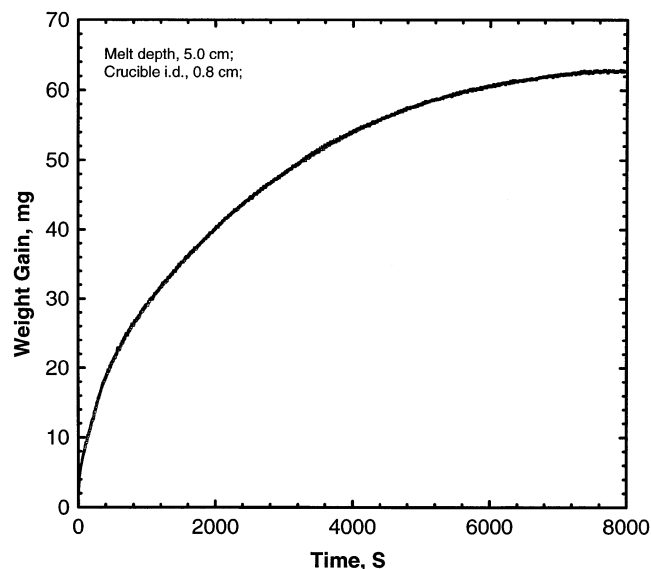

Fig. 5—Weight change during oxidation of liquid iron oxide pre-equilibrated in air and oxidized in pure oxygen at 1615 °C. Melt depth, 5 cm; crucible i.d., 0.8 cm; iron oxide (as Fe_2O_3) weight, 11.863 g; and gas flow rate, 600 SCCM.

flow controllers calibrated by means of soap film burettes. Ferric oxide (99.9 pct) was supplied by BDH Laboratory Supplies (Dorset, England). The preparation of wustite was as follows. A piece of electrolytic iron was hung in the hot zone of a furnace where temperature was brought to 1673 K in N_2. The gas was then changed to a CO-CO_2 mixture with a CO_2/CO ratio of 1.0. The product of the oxidation, liquid wustite, dripped to the water-cooled furnace cap, and was subsequently collected.

III. RESULTS

Preliminary experiments with an empty platinum or magnesia crucible were carried out to check the possible weight change, presumably due to the buoyancy change, when the gases were switched between CO_2-CO mixture, nitrogen, air, and oxygen. No such weight change was observed within the precision of the apparatus. However, when a platinum crucible was used, weight-loss rates of 0.0352 and 0.1426 mg/min were found under the flow of 600 SCCM (standard cubic centimeter per minute) air and oxygen at 1888 K. The higher weight loss rate in oxygen was believed to be due to the phenomenon "oxidation enhanced evaporation," found by Turkdogan et al.[16] for the evaporation of iron, of platinum with the formation of PtO_2. This finding suggested the need to consider the evaporation of platinum at a high temperature. Accordingly, in experiments in which platinum crucibles were used, the steady-state weight-loss rates in pre-equilibrating and oxidizing gas were measured, and the differences were used to make appropriate corrections for the oxygen uptake by the melt during the oxidation.

A. Iron Oxide at Oxidation State between Air and Oxygen

The sample weight change during the oxidation of liquid iron oxide at 1888 K, after appropriate correction for the evaporation of platinum, is shown in Figures 4 and 5. Figure

4 shows the results from two experiments using "short" platinum crucibles. In these experiments, an addition of 7.936 g ferric oxide was made to fill the 11.9-mm-i.d., 15.45-mm-inner height platinum crucible. The melt was equilibrated with air and subsequently oxidized in pure oxygen at a flow rate of 600 SCCM. The total weight gains during oxidation were found to be 46.9 and 45.6 mg from these two experiments. While the reproducibily is fairly good, it should be noted that these values are much higher than those predicted by Darken and Gurry's[14] data, which gives a weight gain of 35.0 mg. In their article, Darken and Gurry admitted the poor precision of their data in the high oxygen range due to the rapid change in compositions of the sample while it cools. This suggests that the "fractional weight gain," described by Eq. [3], is the superior (compare to that described by Eq. [1]) method to evaluate the diffusivity of oxygen. Accordingly, the M_t/M_{max} ratios were calculated from the experimental data, and the diffusivity, D, was then calculated from the data listed in Table I. The average value of the chemical diffusivity of oxygen thus deduced was 4.5 $\times$ 10^{-3} cm^2/s. Figure 6 shows the good fit of the experimental data with the calculated M_t/M_{max} assuming $D = 4.5 \times 10^{-3}$ cm^2/s.

The results of an experiment using a "long" platinum crucible, 8-mm i.d. and 50-mm inner height, are shown in Figure 5. A total of 11.863 g ferric oxide was added to fill the crucible. The chemical diffusivity of oxygen deduced from this experiment was 3.92×10^{-3} cm^2/s. Figure 7 shows the fit of the experimental data with the theoretical predicted M_t/M_{max} assuming $D = 3.92 \times 10^{-3}$ cm^2/s. The results from the two experiments employing different melt depths are in reasonable agreement.

B. Iron Oxide at Oxidation State Close to Iron Saturation

A CO-CO_2 mixture, other than oxygen, was used as the oxidizing gas to achieve the low oxygen potential. To eliminate the effect of the slow interfacial reaction between CO_2
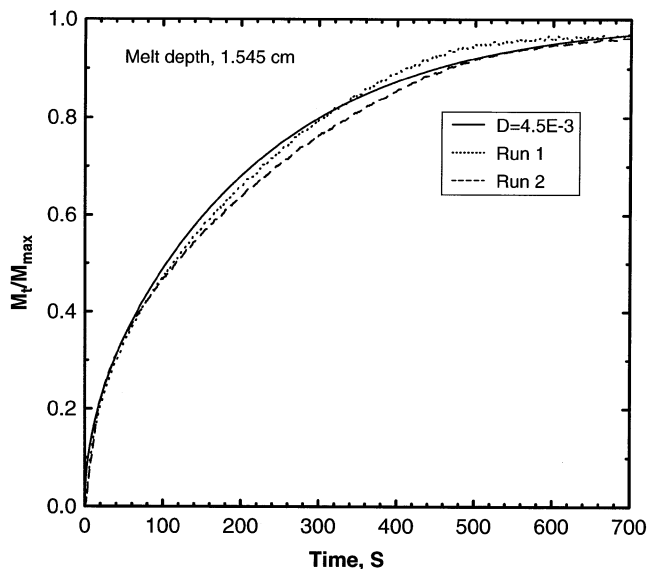
Fig. 6—The fit of experimental data with $D = 4.5 \times 10^{-3}$ cm^2/s for liquid iron oxide pre-equilibrated in air and oxidized in oxygen at 1615 °C. Melt depth, 1.545 cm.

Fig. 8—The sample weight change during the oxidation of liquid iron oxide pre-equilibrated with metallic iron and oxidized in CO$_2$-50 vol pct CO at 1450 °C.
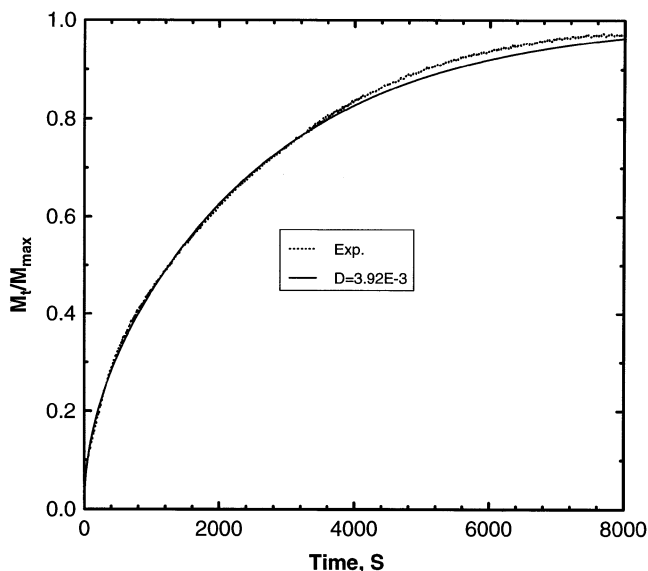

Fig. 7—The fit of experimental data with $D = 3.92 \times 10^{-3}$ cm^2/s for liquid iron oxide pre-equilibrated in air and oxidized in oxygen at 1615 °C. Melt depth, 5 cm.

and the melt, a *steady-state* rather than the non-steady-state method was used in the measurement. Proper experimental parameters (*e.g.*, l and $(C_s - C_0)$) were chosen to ensure that the oxygen flux was small enough to eliminate of the effect of the interfacial reaction and gas-phase mass transfer while being large enough for an accurate measurement.

An electrolytic iron disk, 3 to 5 mm in thickness, was placed in the bottom of a MgO crucible* with an inner

*The Pt crucible can be easily destroyed by FeO at this low-oxygen potential. Iron oxide can quickly creep up the wall of an alumina crucible. Neat experiments were carried out using MgO crucibles. The dissolution of MgO in the melt was slow. In the quenched samples of the longest experiments at 1450°C and 1500 °C, MgO concentrations were found to be 0.86 and 1.56 wt pct, respectively.
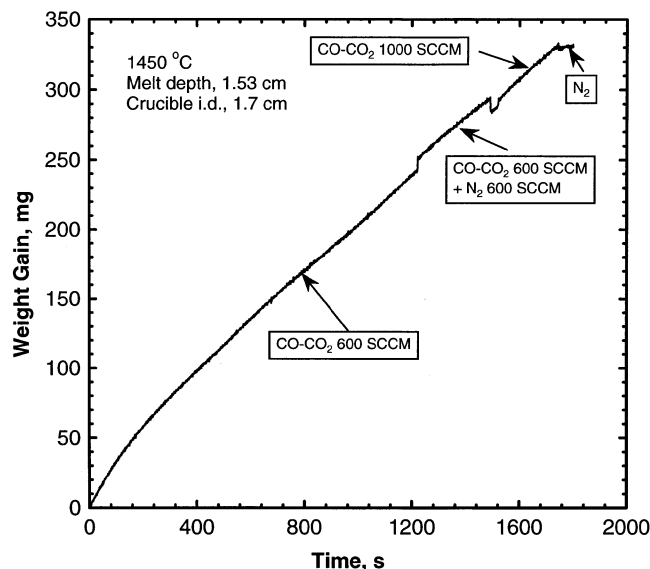
diameter of 17 mm and a height of 28 mm. A predetermined amount (15 g in most of the experiments) of wustite was placed in the crucible on top of the iron disk. The sample was then placed in the furnace and attached to the balance. After heating to the required temperature, the liquid iron oxide was allowed to equilibrate with the metallic iron in an atmosphere of purified nitrogen. The gas was then switched to a CO$_2$-CO mixture in which CO$_2$/CO = 1, and the weight change of the sample was recorded.

Measurements were carried out at three temperatures, 1673, 1723, and 1773 K. At each temperature, a series of experiments was carried out in which the gas composition, gas flow rate, and the melt depth were varied. Figure 8 shows an example of recorded weight change *vs* time curve during the oxidation of the melt at 1723 K. In this experiment, the melt, 15.3 mm in depth, was first oxidized by a CO-CO$_2$ mixture at a total flow rate of 600 SCCM. After the steady state was reached and sufficient data were collected to evaluate the steady-state weight gain rate, nitrogen at a flow rate of 600 SCCM was added to dilute the reaction gas. In the final stage of the oxidation, the gas was changed to a CO-CO$_2$ mixture at a flow rate of 1000 SCCM. The rates of steady-state weight change were 0.1689, 0.1608, and 0.1735 mg/s for the three stages. Less than 5 pct of rate drop was observed when the partial pressure of CO$_2$ was decreased by 100 pct. This indicates that the interfacial chemical reaction was not the rate-controlling step but has a negligible contribution. Similarly, the lack of obvious rate change with the change of gas-flow rate suggests that the mass transfer in the gas phase was not the rate-controlling step.

In another set of experiments, the depth of the melt was varied from 15.3 to 23.78 mm. The results of those experiments are plotted in Figure 9, which shows that the steady-state rate decreases with an increasing depth of liquid iron oxide. The change of the melt depth would have had no effect if the interfacial chemical reaction had been the rate-controlling step. In Figure 10, the rates of weight gain are
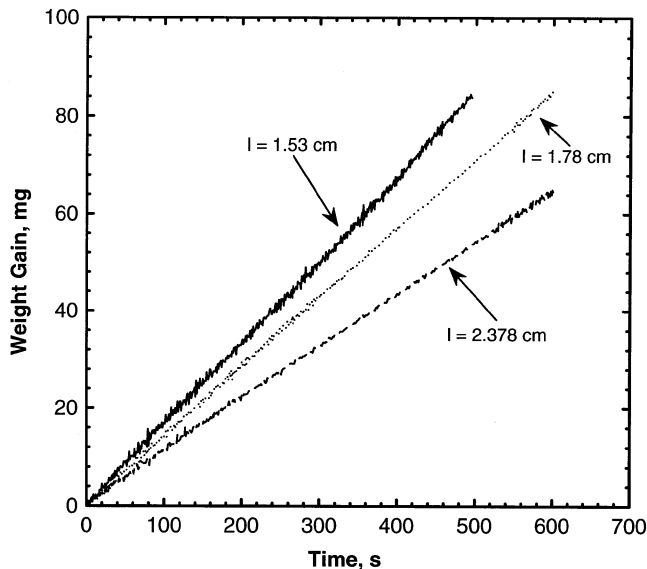
Fig. 9—The sample weight change in the steady-state stage of the oxidation of liquid iron oxide pre-equilibrated with metallic iron and oxidized in CO_2-50 vol pct CO at 1450 °C showing the effect of melt depth.
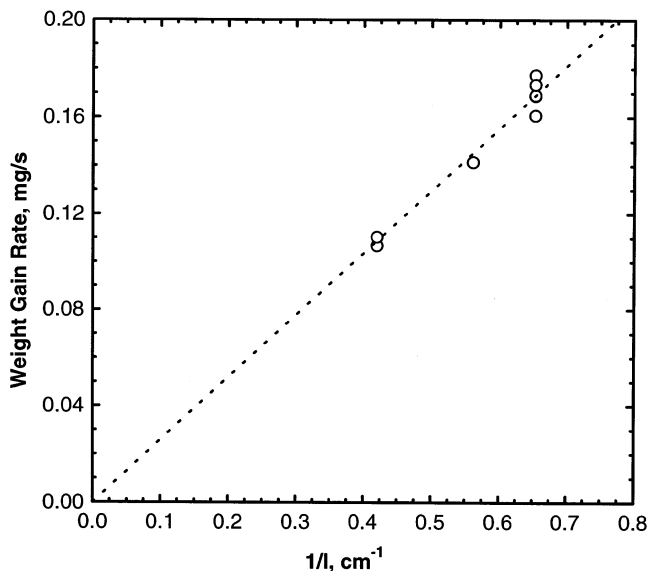

Fig. 10—The steady-state weight gain rate as a function of the melt depth. The melt was oxidized in CO_2-50 vol pct CO at 1450 °C, while its bottom was in contact with metallic iron.

plotted against the reciprocal of melt depth. The results show good linearity with the line crossing origin, which is in good accordance with Eq. [5]. This result is further evidence that oxygen diffusion in the melt, rather than the interfacial chemical reaction or gas-phase mass transfer, is the rate-controlling step.

The diffusivity, D, was deduced from the experimentally measured steady-state weight-gain rate, according to Eq. [5]. The results are listed in Table II. The concentrations, C_s and C_0, were calculated according to Eq. [2]. The Fe^{3+}/Fe^{2+} ratios in the liquid iron oxide in equilibrium with metallic iron and a gas of $CO_2/CO = 1$ were taken from the data of Darken and Gurry.[14] Unlike those for high oxygen potentials, Darken and Gurrys' iron-oxygen equilibrium data for

low-oxygen potentials have been proved by many studies to be very accurate. The density of the melt was taken from the data of Mori and Suzuki.[17] It is noted that there are significant differences in literature[18,19] values for the density of liquid Fe_xO. Fortunately, the difference for the density of the melt near iron saturation is reasonably small.[19]

Equation [6] has also been used to evaluate the diffusivity from the experimental data. The results are in broad agreement with the values of diffusivity evaluated from the steady-state rate. However, the scatter is large, possibly due to the effect of interfacial chemical reaction in the initial stage of oxidation and the nonuniformity of the initial concentration in the melt.

The Arrhenius plot (Figure 11) shows the effect of temperature on the chemical diffusivity of oxygen in liquid iron oxide. The data are consistent with the equation

$$\log D = -6220/T + 1.12 \qquad [7]$$

with an overall scatter of about ±20 pct in values of D.

C. Calcium Ferrite Fe_2O_3-21.43 Wt Pct CaO (Fe/Ca = 2.5665)

Similar measurements to those described in Section III–A were carried out for this slag at temperatures between 1573 and 1873 K. In a series of experiments using short crucibles (15.45 mm in height), about 6.85 g of slag was used to fill the crucible. The slags were initially equilibrated with a 10 pct air-N_2 mixture and subsequently oxidized in pure oxygen. Figure 12 shows the weight gain of the sample during the oxidation in these experiments. The values of the diffusivity of oxygen deduced from these results are listed in Table III. From redox data for the CaO-Fe_xO system, the predicted maximum weight change can be calculated. Calculation was carried out based on the correlation[20]

$$\log \frac{Fe^{3+}}{Fe^{2+}} = 0.17 \log P_{o_2}$$
$$+ 0.018 \text{ (wt pct CaO)} + \frac{5500}{T} - 2.52 \qquad [8]$$

The calculated results and the measured values are listed in the second and third rows in Table III. Reasonable agreement was reached.

Experiments using longer crucibles, with a melt depth of 50 mm, were also conducted. The melts were initially equilibrated with air and subsequently oxidized in pure oxygen. The deduced diffusion coefficients are 3.42×10^{-3}, 4.31×10^{-3}, and 5.85×10^{-3} cm^2/s for temperatures of 1573, 1673, and 1773 K, respectively. The Arrhenius plot, Figure 13, shows the effect of temperature on the chemical diffusivity of oxygen in this calcium ferrite with Fe/Ca = 2.5665. The data are consistent with the equation

$$\log D = -1760/T - 1.31 \qquad [9]$$

IV. DISCUSSION

A. Significance of the Rate of the Interfacial Chemical Reaction on Diffusivity Measurement

The values of the chemical diffusivity of oxygen in liquid iron obtained from the present study are of the order of 10^{-3}

Table II. Results of Steady-State Measurements

| Experiment Number	Temperature, K	Depth, cm	Oxidation Gas, Pct	Flow rate, SCCM	Weight Gain Rate, 10^{-5} g cm^{-2} s^{-1}	D, 10^{-3} cm^2/s
1	1673	1.42	CO_2-50CO	1000	6.077	2.46
2	1673	1.42	CO_2-25CO-50N_2	1200	5.706	2.31
3	1673	1.42	CO_2-50CO	600	6.6	2.67
4	1673	1.42	CO_2-50CO	300	6.423	2.5
5	1673	1.42	CO_2-50CO	600	6.546	2.65
6	1723	1.53	CO_2-50CO	600	8.0	3.36
7	1723	1.53	CO_2-25CO-50N_2	1200	7.628	3.2
8	1723	1.53	CO_2-50CO	600	7.619	3.2
9	1723	1.53	CO_2-25CO-50N_2	1200	7.254	3.05
10	1723	1.53	CO_2-50CO	1000	7.827	3.29
11	1723	1.78	CO_2-50CO	1000	6.383	3.12
12	1723	2.378	CO_2-50CO	600	4.813	3.14
13	1723	2.378	CO_2-50CO	1000	4.976	3.25
14	1773	1.566	CO_2-50CO	1000	11.116	4.51
15	1773	1.573	CO_2-50CO	1000	10.994	4.44
16	1773	1.573	CO_2-50CO	600	8.964	3.62
17	1773	1.573	CO_2-25CO-50N_2	1200	9.46	3.82
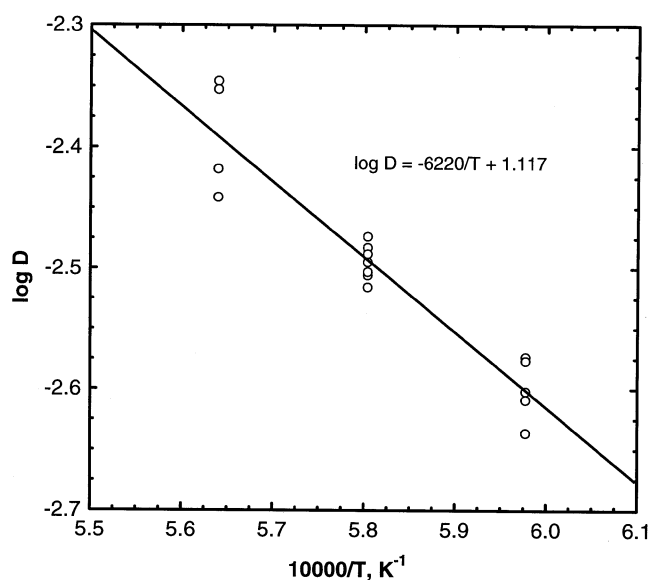
Fig. 11—The chemical diffusivity of oxygen in liquid iron oxide at oxidation state near iron saturation as a function of temperature.
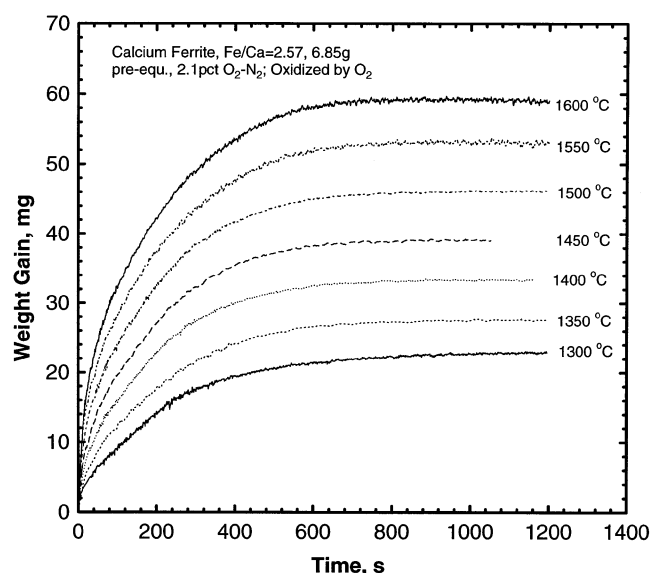

Fig. 12—Sample weight gain during the oxidation of a calcium ferrite at temperatures from 1300 °C to 1600 °C. The melt was pre-equilibrated in 10 vol pct air-N_2 mixture and subsequently oxidized in pure oxygen.

cm^2/s. They are in reasonable agreement with the most recent data obtained by Sayadyaghoubi et al.[8] but are one or two orders of magnitude higher than the older data of Mori and Suzuki[7] and Grieveson and Turkdogan.[6] The difference is believed to be due to the effect of the interfacial chemical reaction.

The gas-slag reaction was employed in all studies. In deriving of the value of the oxygen diffusivity from the measured rate (in the from of either concentration change or sample weight change), the oxygen potential of the slag at the gas-slag interface was *assumed* to be the same as that of the bulk gas throughout the oxidation or reduction period. In fact, these two potentials must be different as long as the reaction is proceeding because of the resistance of the mass transfer in the gas phase and the interfacial chemical reaction. The magnitude of the potential difference depends on the rate, the mass transfer coefficient in the gas, and the chemical

reaction rate constant. At a given rate, the potential difference is smaller when the gas-phase mass transfer coefficient and chemical reaction rate constant are larger. Smaller potential differences make the actual situation closer to the *assumption* and, thus, leads the derived diffusivity being closer to the 'true,' usually larger value.

In the two older studies (References 6 and 7), the melt was pre-equilibrated with a gas mixture of CO_2-CO and oxidized or reduced by CO_2-CO mixtures with different CO_2/CO ratios. At that time, the rate of interfacial chemical reaction between liquid iron oxide and CO_2-CO gases had not been established, and the rate was assumed to be controlled by the liquid-phase diffusion. With more accumulated data[9,10] on the chemical reaction rate at the interface between a slag and CO_2-CO gases, Belton[11] has analyzed Grieveson and Turkdogan's[6] data and has shown that the

Table III. Results for the Oxidation of 6.85 g Slag Sample (Fe$_x$O-CaO) from 10 Pct Air-N$_2$ to Oxygen

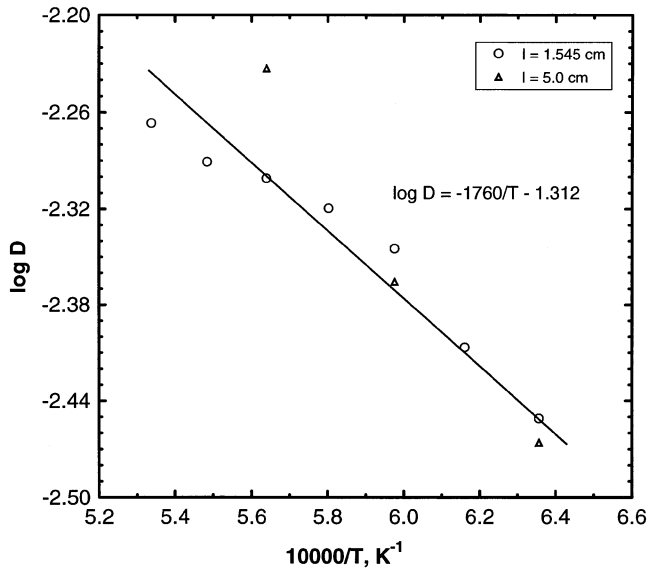| T, K	1572	1623	1673	1723	1773	1823	1873
$\Delta W_{cal.}$, mg	20.23	25.03	30.33	36.03	42.01	48.11	54.17
$\Delta W_{meas.}$, mg	23.5	27.8	33.5	39.5	46.3	53.2	59.3
D, 10^{-3} cm^2/s	3.54	3.92	4.52	4.79	5.0	5.12	5.41

Fig. 13—The chemical diffusivity of oxygen in 21.43 wt pct CaO-Fe$_2$O$_3$ as a function of temperature.

measured rate was in close agreement with the rate calculated for the gas-slag chemical reactions. Another fact is that Grieveson and Turkdogan observed that the diffusivity evaluated from their reduction experiments was 10 to 20 pct higher than that from oxidation. This might be the result of faster reduction than that of oxidation in their experiments. The interfacial chemical reaction rate between liquid iron oxide and CO$_2$-CO gases is given by[5]

$$v = k_a^0 \left(\frac{P_{CO_2}}{P_{CO}}\right)_{eq}^{-0.8} \left[P_{CO_2} - P_{CO}\left(\frac{P_{CO_2}}{P_{CO}}\right)_{eq}\right] \quad [10]$$

for the oxidation, and

$$v = k_a^0 \left(\frac{P_{CO_2}}{P_{CO}}\right)_{eq}^{0.18} \left[P_{CO} - P_{CO_2}\left(\frac{P_{CO_2}}{P_{CO}}\right)_{eq}^{-1}\right] \quad [11]$$

for the reduction, where $(P_{CO_2}/P_{CO})_{eq}$ is the value of the ratio that would be in equilibrium with the melt, and k_a^0 is the reaction rate constant at CO$_2$/CO = 1.0. For Grieveson and Turkdogan's[6] oxidation and reduction experiments of CO$_2$/CO ratio changed between 10 and 75, the initial chemical reaction rates were calculated, according Eqs. [10] and [11] to be 0.136 k_a^0 and 0.172 k_a^0 for the oxidation and reduction, respectively. Because the kinetics were dominated by the chemical reaction rather than by diffusion, it was not abnormal to obtain a higher reduction rate than oxidation rate.

The previously mentioned treatment is more significant when it is used to analyze Mori and Suzuki's[7] data. In their oxidation experiments, they observed a higher rate in the lower oxidation range. They attributed this phenomenon to the dependence of oxygen diffusivity on the oxidation state of the melt and concluded that the diffusivity decreased from about 4×10^{-4} to 5×10^{-5} cm^2/s as Fe^{3+}/ΣFe increased from 0.12 to 0.42 at 1823 K. In their experiment for Fe^{3+}/ΣFe of 0.12, the melt was pre-equilibrated with an atmosphere of CO$_2$/CO = 0.38 and oxidized in an atmosphere of CO$_2$/CO = 1.2. The initial rate of the chemical reaction, calculated according to Eq. [10] is 0.808 k_a^0. Similar calculation for Fe^{3+}/ΣFe of 0.42 yields an initial rate of the chemical reaction of 0.078 k_a^0. The tenfold decrease of the chemical reaction rate almost coincides with the eightfold of decrease in the calculated diffusivity. This in itself is evidence that in Mori and Suzuki's[7] measurements the interfacial chemical reaction dominated the kinetics. The values of diffusivity should be higher than the reported ones. Also, the reported strong dependence of oxygen diffusivity on the oxidation state of the melt is likely to be a misleading conclusion.

In the study by Sayadyaghoubi et al.[8] and the high oxygen potential range measurements of the present study, pure oxygen was used as the oxidizing gas. No data are available for the interfacial chemical reaction between oxygen and liquid iron oxide. The oxygen dissociation rate constant on Cu$_2$O at 1273 K was measured by Stotz[21] to be about 3×10^{-5} mol cm^{-2} s^{-1} atm^{-1}. The dissociation rate constant of CO$_2$ on Cu at 1273 K, being independent of the oxygen potential, was determined by Grabke[22] to be 1.8×10^{-7} mol cm^{-2} s^{-1} atm^{-1}. The dissociation rate constant of CO$_2$ on wustite and magnetite at 1256 K was found to be in the order of 10^{-9} to 10^{-8} mol cm^{-2} s^{-1} atm^{-1} depending on the oxygen potential.[23] From these values, it is expected that the rate of O$_2$-liquid iron oxide reaction is at least two or three orders faster than that of CO$_2$-liquid iron oxide. In the recent study (Reference 8) and present study, the effect of gas-melt interfacial chemical reaction was minimized by using pure oxygen as the oxidizing gas. The surface concentration of the melt was, thus, closer to the one in equilibrium with the gas during the oxidation. This made the deduced diffusivity from these two studies to be closer to the "true" value.

It should be noted that in the measurement of the oxygen diffusivity in liquid iron oxide at low-oxygen potential, as presented in Section III–B, CO$_2$-CO mixtures were used as oxidizing gases. The steady-state rate was used to calculate the diffusivity. At a known steady-state rate, it is possible to calculate the oxygen potential of the melt at the gas-slag interface from Eq. [10]. The calculated values for experiments presented in Table II were between 0.9 and 0.95 in terms of the (P_{CO_2}/P_{CO}) ratio. If these values, instead of the (P_{CO_2}/P_{CO}) ratio in the gas phase (i.e., 1), are used in the evaluation of diffusivity, the deduced D will be about 5 pct higher than those reported in Table II.

B. *The Effect of Composition on Diffusivity in Liquid Iron Oxide*

Diffusivity is often found to depend on concentration. The concentration of oxygen (and iron) in liquid iron oxide varies, in a wide range, with the oxygen potential and temperature. To study the dependence of diffusivity on the oxidation state in liquid iron oxide is one of the intentions of the present work. To do this, many measurements need to be carried out stepwise in the possible oxygen potential range. The oxygen potential in the system can be controlled conventionally by the CO_2/CO ratio in the gas phase. Unfortunately, due to the slow chemical reaction between liquid iron oxide and CO_2-CO gases, the oxidation or reduction by these gases may be dominated by the interfacial chemical reaction as discussed in Section IVA. In the present study, the diffusivity of oxygen in liquid iron oxide at two extreme oxygen potentials, with one close to iron saturation and the other close to pure oxygen, was measured. At the high oxygen potential, the value of deduced D was $4.2 \pm 0.3 \times 10^{-3}$ cm^2/s at 1888 K. At the low oxygen potential, measurements were carried in the temperature range of 1673 to 1773 K. From this series of data, an extrapolation gives a value of 6.7×10^{-3} cm^2/s at 1888 K. It appears that the diffusivity of oxygen in liquid iron oxide decreases with an increase of oxidation state of the melt. However, it should be noted that this dependence is not very strong; only about 40 pct decrease when the oxygen potential is increased from 10^{-7} to 1 atm. Because of the effect of the surface reaction, it seems extremely difficult to firmly establish this dependence by directly measuring the chemical diffusivity at different oxygen potentials. Alternatively, the measurements of tracer diffusion coefficient, where no gas-slag interfacial reaction takes place, should be carried out at various oxygen potentials. The chemical diffusivity can then be calculated by applying the Darken equation because the thermodynamics of iron-oxygen system have been firmly established.

C. *The Effect of CaO Addition on the Diffusivity in Iron Oxide*

At high-oxygen potentials between air and pure oxygen, the measured chemical diffusivity of oxygen in a calcium ferrite with Fe/Ca ratio of 2.57 at 1873 K was 5.4×10^{-3} cm^2/s, about 30 pct higher than that for pure iron oxide. At high-oxygen potential, a substantial amount of iron in liquid iron oxide is in the higher (+3) valence state. Considering the acidic nature of ferric ion, in the form of $Fe_2O_5^{4-}$ or $Fe_2O_3^{3-}$,[24] the free oxygen in the melt is expected to increase with the addition of calcium oxide. Accordingly, the diffusivity of oxygen in calcium ferrite is expected to be higher than that of iron oxide.

V. CONCLUSIONS

1. The chemical diffusivities of oxygen in liquid iron oxide and a calcium ferrite have been determined by directly measuring the oxygen uptake during the oxidation.
2. The chemical diffusivity of oxygen in liquid iron oxide at oxygen partial pressure between 0.21 and 1 atm was determined to be $4.2 (\pm 0.3) \times 10^{-3}$ cm^2/s at 1888 K. That in iron oxide at oxidation state close to iron saturation was established to be given by the empirical expression $\log D = -6220/T + 1.12$ for temperatures between 1673 and 1773 K. For the calcium ferrite (Fe/Ca = 2.57) at oxygen potential between air and oxygen, the diffusivity of oxygen was found to be given by $\log D = -1760/T - 1.31$ for temperatures between 1673 and 1873 K.
3. It appears that the chemical diffusivity of oxygen in liquid iron oxide decreases with oxidation state. The decrease is approximately 40 pct between iron saturation and equilibrium with oxygen at 1 atm. The strong dependence found by Mori and Susuki[7] was demonstrated to be the results of the effect of interfacial chemical reaction.
4. The chemical diffusivity of oxygen increased when calcium oxide was added to iron oxide.
5. The measurements of previous studies, which generated the values of chemical diffusivity two orders of magnitude lower than the present results, were demonstrated to be dominated by the interfacial chemical reaction rather than liquid-phase diffusion.

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